**Supporting Information**

**Adsorption Isotherm and Kinetic Modelling of a Novel Procedure for the Physical Modification of Silica Gel using Aqueous Solutions of an N2O2Tetradentate Ligand, 4,4′-(1,2-ethanediyldinitrilo)bis-(2-pentanone) for Solid Phase Extraction and Preconcentration of Ni(II) Ion**

**Nwabue, F. I.\* and Itumoh E. J.**

Department of Industrial Chemistry, Ebonyi State University, PMB 053, Abakaliki, Nigeria

\*Author for correspondence, E-mail: [ikennanwabue@gmail.com](mailto:ikennanwabue@gmail.com) Phone: +234 803 7059 082

**Experimental**

***Instrumentation***

Genesys 10s (Thermo Fisher Scientific Inc., Madison WI, USA) UV-vis spectrophotometer was used to obtain the electronic spectra of EDDBP. Hach Sension 3 (Hach Company, Loveland, Colo. USA) pH meter was used for the pH determination. Infra-red spectra of EDDBP were recorded using IR 100 series (Thermo Electron Corporation). NMR data were obtained on Varian Mercury YH200 MHz NMR spectrometer. Magnetic stirrohotplate (Remi Equipment, Mumbai India) was used for stirring. Bruker® D8 Discover diffractometer, equipped with a Lynx Eye detector, under Cu-Kα radiation (λ = 1.5405 Å), and ASAP-2020 adsorption apparatus (Micromeritics) of the Nanotechnology and Innovation Centre, Rhodes University, South Africa were used for XRD measurements and the determination of pore textural properties of the EDDBP-modified SG respectively.

# ***Reagents and materials***

The SG (70 – 230 μm) was purchased from Riedel de Haën Hannover, Germany. Acetylacetone (99% purity) was purchased from Merck - Schuchardt, Honenbrunn Ian Munchen. Ethylene diamine (99% purity) was purchased from Fluka Analytical, Sigma Aldrich St. Louis, MO USA. All other reagents used were purchased from BDH Chemicals Co. Ltd, Poole England. All the reagents were of analytical grade. Except for SG, all other reagents were used without further purification. The ligand (EDDBP) was prepared as previously reported[1], characterized by UV-vis, IR and NMR analyses, and was used as 2% aqueous solution. The silica gel was activated following the procedure described elsewhere [2].

# ***Preparation of buffer solutions (pH 1 – 12)***

Clark and Lubsprocedures[3] were used to prepare buffer solutions (pH 1 – 12). These were prepared by addition of standard solutions of hydrochloric acid or sodium hydroxide to portions of stock solutions of KCl, KH2PO4, K2HPO4, or H3BO3, followed by suitable dilution with DDW. Other buffer systems of acetic acid-sodium acetate, citric acid-trisodium citrate, oxalic acid-sodium oxalate, ammonia-ammonium chloride and sodium dihydrogen phosphate-disodium hydrogen phosphate were prepared as described elsewhere[4]using 0.2 *M* solutions of the additives in suitable ratios and adjusting to the desired pH where necessary with dilute HCl or NaOH (NH3 was used for ammonia-ammonium chloride buffer).

# ***Adsorption experiments***

The effects of pH, contact time, mineral acids, initial amount of EDDBP and the total volume of the ligand solution on the adsorption of EDDBP on the SG surface were determined as follows:

*Effect of pH*: The activated SG (0.1 g) was weighed out separately into 12 different extraction bottles and added 2 mL of the EDDBP solution. The mixture was made up to 5 mL with the appropriate pH buffer solution, stirred for 5 min and then filtered. The unadsorbed EDDBP on the SG residue was washed off into the filtrate with 1 mL of DDW. The filtrate was adjusted to the working pH and then made up to 10 mL using the particular pH. The amount of EDDBP in the filtrate was determined spectrophotometrically at 240 nm against the reagent blank. The SG residue was dried, weighed and the amount of EDDBP adsorbed on the SG surface determined gravimetrically by mass balance.

*Effect of contact* time: The mixture of activated SG (0.1 g) and 2 mL of EDDBP solution was made up to 5 mL with pH 1 and was equilibrated for 2, 3, 5, 10, 30 and 90 min in separate bottles. The amount of EDDBP in the filtrate and adsorbed on the SG residue was then determined as previously described.

*Effect of acids, initial EDDBP amount and volume*: The experiments to determine the effects of mineral acids (0.0001 – 2.0 M), the initial amount of EDDBP (2 – 100 mg) and total volume of the EDDBP solution (5 – 100 mL) were similarly performed as described above.

# ***Characterisation of EDDBP–modified SG***

The EDDBP–modified SG samplewas placed on a zero background silicon wafer slide and the XRD data collected over the 2θ = 0-1000 range, scanning at 0.0100 min-1 and 192 s per step[5].

The pore textural properties of the EDDBP–modified SG sample, including the specific Brunauer–Emmet–Teller (BET) surface area, pore size distribution, nitrogen adsorption and desorption isotherms, were measured on an adsorption apparatus. The BET method was utilized to calculate the specific surface area of the sample using the non-local density functional theory (NLDFT) model. The pore volume was derived from the sorption curves. The sample was first dried under vacuum (10-4 bar) at 400 K for 20 h and then degassed under ultrahigh vacuum (10-9 bar) at 393 K for 16 h. The sample was back-filled with nitrogen, transferred to the analysis system, and then again degassed under ultrahigh vacuum at 373 K overnight. The BET surface area was calculated based on relative pressures 0-12 mmHg. The micro pore analysis was obtained from the nitrogen adsorption and desorption data[6].

# ***Theoretical models of the adsorption process***

*The Langmuir isotherm*

The Langmuir isotherm is represented by Eq. (1):

(1)

The equation can be changed to a linear form as Eq. (2).

(2)

where *qe* (mg/g) is the amount of adsorbate on the adsorbent at equilibrium, *qmax* (mg/g) is the theoretical monolayer capacity, *KL* is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption, and *Ce* (mg/mL) is the equilibrium solution concentration of the adsorbate. The linear plot of (𝐶𝑒/𝑞𝑒) against the equilibrium concentration (𝐶𝑒) is used to show if an adsorption process obeys the Langmuir model. The values of the constants *KL*and 𝑞max are obtained from the slope and intercept of the plot[7].

*The Freundlich isotherm*

The Freundlich adsorption isotherm model is used for adsorption onto heterogeneous surfaces [8] and predicts the relationship between the solute concentration on the surface of an adsorbent to the solute concentration in the liquid with which it is in contact. The Freundlich isotherm is given as Eq. (3):

(3)

The equation can be linearized and the temperature dependent constants *KF* and 1/𝑛found by linear regression as Eq. (4):

(4)

where *qe*represents the amount adsorbed per amount of adsorbent at equilibrium (mg/g), *Ce*represents the equilibrium solution concentration (mg/mL) of the adsorbate, and *KF* and *n* are Freundlich constants which represent the adsorption capacity and the adsorption strength respectively. The parameters are obtained from the intercept and slope of the linear plot of log(*qe*) versus log(*Ce*). The value of 1/*n* describes how favourable the adsorption is and the extent of heterogeneity of the adsorbent surface [8].

*The Temkin Isotherm model*

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. By ignoring the extremely low and large values of concentration, the isotherm model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmically with surface coverage due to adsorbate/adsorbate interactions [9, 10]. The Temkin isotherm has been used in the form of Eq. (5) and modified into (6):

= ln( (5)

= ln( + ln() (6)

But if *B* = , Eq. 6 will become:

= *B* ln( + *B*ln() (7)

where *A*t = Temkin isotherm equilibrium binding constant (L/g), *b* = Temkin isotherm constant (kJ/mol), R = universal gas constant (8.314 J/mol/K), T = Temperature at 301 K and *B* = a constant related to heat of sorption in kJ/mol. Temkin isotherm is obtained by plotting the quantity sorbed (*q*e) against ln(*C*e), and the constants are determined from slope and intercept of the curve.

*Dubinin–Radushkevich isotherm model*

Dubinin–Radushkevich isotherm model is applied to express the mechanism of adsorption with a Gaussian energy distribution into a heterogeneous surface. This model is often successfully fitted with the intermediate range of data concentrations and high solute activities[9] in which the linear equation and constant are as given in Eqs. 8-10:

= exp(−*Bε*2) (8)

ln( = ln(− (*Bε*2) (9)

*ε* = *RT* ln (10)

where *q*s is Dubinin–Radushkevich isotherm constant related to the degree of sorption on the sorbent surface and *B* is denoted as the isotherm constant. The approach is usually used to specify the physicochemical adsorption of an adsorbate with its average free energy (*E*) of sorption per adsorbate molecule when it is moved to the solid surface from initial solution infinity and can be calculated using Eq. 11.

*E* = (11)

*The pseudo-first-order-kinetic model*

Sorption kinetic rate equation as given in Eq. (12) can be used to represent an adsorption system that follows the pseudo-first-order-kinetics.

(12)

where *k*1 is the rate of sorption (min-1), *q*e the amount of adsorbate adsorbed onto the adsorbent at equilibrium (mg/g) and *q* is the amount of adsorbate adsorbed at any time (mg/g). Integrating Eq. (16) for boundary conditions *t* = 0 and *t* = *t* and *q* = 0 and *q* = *q*, gives Eq. (13)[11]:

(13)

*The pseudo-second-order-kinetic model*

For any adsorption system that follows the pseudo-second-order-kinetics, the adsorbate was assumed to get adsorbed onto two surface sites[11]. Thus, the adsorption kinetics for an adsorbate onto an SG is given as Eq. (14):

(14)

where (SG)0 is the number of active sites available on the SG surface and (SG)*t* represents the number of active sites occupied on the silica gel at any time.

Thus, rewriting the kinetic rate equation gives Eq. (15):

(15)

where *q* is the amount of adsorbate adsorbed at any time (mg/g), *q*e the amount of adsorbate adsorbed onto SG at equilibrium (mg/g) and *k*2 is the rate of sorption (g/mg min). Eq. (15) can be rearranged to give Eq. (16) as:

(16)

At boundary conditions of *q* = 0 and *q* = *q* and *t* = 0 and *t* = *t*, Eq. (16) can be integrated to give Eq. (17)[11]:

(17)

Eq. (17) gives the pseudo-second-order adsorption rate law. A previous study [12]had suggested that physisorption processes are consistent with the pseudo-second-order kinetic model.

*Elovich’s kinetic model*

Elovich’s kinetic law of chemisorption is another rate equation based on the adsorption capacity[13]. The rate of adsorption of EDDBP onto SG decreasing exponentially with an increase in the amount of EDDBP adsorbed is given as Eq. (18) [13, 14]:

= (18)

where *q* is the amount of EDDBP adsorbed during the time *t*, αir the initial adsorption rate, and *β* is the desorption constant during any one experiment. To simplify Elovich’s equation, Chien and Clayton [13] assumed that *β*αir*t*>> 1 and by applying the boundary conditions of *q* = 0 at *t* = 0 and *q* = *q* at *t* = *t*, then Eq. (18) becomes Eq. (19):

*q* = 1/αirln(*β*αir) + 1/αirln(*t*) (19)

Thus, the constants can be obtained from the slope and the intercept of a straight-line plot of *q* against ln(*t*).

*Validity of theoretical isotherm and kinetic models*

The applicability of the theoretical isotherm and kinetic models in describing the adsorption process of EDDBP onto SG was further validated using a normalised standard deviation, Δ*q* (%)[15]. The statistical determination Δ*q* (%) is based on a percentage of the sum of the difference between experimental and theoretical adsorption capacities from the isotherms, or kinetic models, of which was divided by the experimental adsorption capacity and squared, and subsequently divided by the difference between the number of points and unity. It is defined as Eq. (20):

= 100 (20)

where *N* is the number of data points, *q*e,exp and *q*e,cal (mg/g) are the experimental and calculated adsorption capacity, respectively. A low value of Δ*q* (%) indicates that experimental data fit better into the model. In order to confirm the best-fit model for an adsorption system, there is a need to analyse the data set using the Δ*q* (%), combined with the values of the determined regression coefficient (*R*2)[16].

The temperature dependence of adsorption process is associated with changes in several thermodynamic parameters such as standard free energy (ΔGo), enthalpy (ΔHo) and entropy (ΔSo) of adsorption[9]. Standard free energy (ΔGo) can be calculated using Eq. (21)[12]:

ΔGo = −*RT*ln*b* (21)

where *R* is the universal gas constant, *T* the temperature (K) and *b* the Langmuir constant (*b* = *K*L×*q*max). In this work, experiments were carried out at constant temperature (301 K) and hence only the standard free energy was evaluated using Eq. 21.

# ***Characterisation of EDDBP***

The synthesized EDDBP was characterized based on melting point, UV-vis, IR and NMR spectra. The melting point was 381±1 K. We have previously noted[17, 18]that EDDBP exists in three tautomeric forms, keto-imine, enol-imine and keto-amine (Scheme 1). The UV-vis spectra of EDDBP showed that it has maximum absorption at 321.9 nm with a shoulder at 237 nm and molar absorptivities of 5.3 × 104 and 1.1 × 104 L mol−1 cm−1 respectively. These have been attributed to *n* → *π*\* and *π* → *π*\* transitions respectively.

Table 1 shows the essential peaks of the FTIR spectra of EDDBP. The peak at 3100 cm−1 was due to hydrogen-bonded OH or NH in EDDBP. The weak band at 2820 cm−1 was attributed to CH2 or CH3 absorption. The peak at 1625 cm−1 was associated with stretching frequency of the C=O carbonyl group. The presence of a broad peak at 1590 cm−1and a strong peak at 1500 cm−1 were respectively assigned to C=C andC=Nvibrations characteristic of Schiff’s bases.

The proton NMR data of EDDBP in CDCl3 with TMS as an internal reference is given in Table 2. The sharp doublet at 1.87 integrated for 12 protons was assigned to the slightly non-equivalent CH3C−N and CH3C−O protons. The 4 H, showing astriplet at 3.39 ppm is due to the ethylene bridge protons whereas the singlet at 4.91 (2H) was attributed to the vinyl hydrogens. This is related to the broadband at 10.60 integrated for 2H which likely arose from the strongly hydrogen-bonded enolic form. This shows that in CDCl3 solvent the structural form of EDDBP is strongly hydrogen bonded.

Tables

Table 1

Infrared absorption bands (cm−1) of EDDBP as nujol mull

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Assignment | −OH, from H2O | OH | NH | CH3,  CH2 | C=Ο | C=C | C=N | C−CH3 | C−N | C−O | C=C |
| EDDBP | - | 3100(br) | 2900(br) | 2820(w) | 1625(w) | 1590(br) | 1500(s) | 1440(w)  1355(w) | 1340(s) | 1270(s)  1125(w) | 920(w) |

*Note: s = strong, w = weak, br = broad*

Table 2

Proton magnetic resonance data of EDDBP in CDCl3 relative to TMS reference

|  |  |
| --- | --- |
| Signal (ppm) | Assignment |
| 10.60 (br) 2 H | Sym. O-H, hydrogen-bonded |
| 4.91 (s) 2 H | Sym. =C-H, methyne protons |
| 3.39 (t) 4 H | −CH2− CH2, methylene bridge protons |
| 1.87 (d) 12 H | Sym. CH3C − O(N) non-equivalent |

*Note: d = doublet, t = triplet, br = broad, s = singlet, sym = symmetrical*



Scheme 1: The three tautomeric forms of EDDBP

**References**

|  |  |
| --- | --- |
| [1] | Nwabue, F. I.; Okafo,E. N. (1992). Studies on the Extraction and Spectrophotometric Determination of Ni(II), Fe(II); V(IV) with Bis(4-Hydroxypent-2-ylidene)diaminoethane, *Talanta,* 39(3): 273-280. |
| [2] | Fan, J.; Qin, Y.; Ye, C.; Peng, P.;Wu,C. (2008). Preparation of the Diphenylcarbazone-functionalized Silica Gel; Its Application to On-line Selective Solid-phase Extraction; Determination of Mercury by Flow-injection Spectrophotometry, *Journal of Harzardous Materials,* 150: 343-350. |
| [3] | Bower, V. E.; Bates,R. G. (1955). pH Values of the Clark; Lubs Buffer Solutions at 250C, *Journal of Research of the National Bureau of Standards (Research Paper 2619),* 55(4): 197-200. |
| [4] | American Chemical Society (ACS), *Reagents, Buffers; Indicators*, American Chemial Society, 2014: 1-5. |
| [5] | Nwaji, N.; Jones, B.; Mack, J.; Oluwole, D. O.; Nyokong,T. (2017). Nonlinear Optical Dynamics of Benzothiazole Derivatized Phthalocyanines in Solution, Thin Films and When Conjugated to Nanoparticles, *Journal of Photochemistry; Photobiology A: Chemistry,* 346: 46-59, 2017. |
| [6] | Neti,V. S. P. K.; Wang, J.; Deng, S.; Echegoyen, L. (2015). High and Selective CO2 adsorption by a Phthalocyanine Nanoporous Polymer, *Journal of Materials Chemistry A,* 3: 10284-10288. |
| [7] | Sathyanarayana, B.; Seshaiah,K. (2011). Kinetics and Equilibrium Studies on the Sorption of Manganese(II); Nickel(II) onto Kaolinite; Bentonite, *E-Journal of Chemistry,* 8(1): 373-385, 2011. |
| [8] | Desta,M. B. (2013). Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (*Eragrostis tef*) Agricultural Waste, *Journal of Thermodynamics,* 2013: 1-6. |
| [9] | Akbartabara, I.; Yazdanshenasa, M. E.; Tayebib, H. A.; Nasirizadeha,N. (2017). Physical Chemistry Studies of Acid Dye Removal from Aqueous Media by Mesoporous Nano Composite: Adsorption Isotherm, Kinetic; Thermodynamic Studies, *Physical Chemistry Research,* 5(4): 659-679. |
| [10] | Gruszecka-Kosowska, A.; Baran, P.; Wdowin, M.; Franus,W. (2017). Waste Dolomite Powder as an Adsorbent of Cd, Pb(II), and Zn from Aqueous Solutions, *Environmental Earth Sciences,* 76: 521-533. |
| [11] | Kumar,K. V. (2006). Linear and Non-linear Regression Analysis for the Sorption Kinetics of Methylene Blue onto Activated Carbon, *Journal of Hazardous Material,* B137: 1538-1544. |
| [12] | Zhang, B.; Li, F.; Wu, T.; Sun, D.; Li,Y. (2015). Adsorption of p-nitrophenol from Aqueous Solutions using Nanographite Oxide, *Colloids and Surfaces A: Physicochemical; Engineering Aspects,* 464: 78-88. |
| [13] | Ho,Y. S. (2006). Review of Second-order Models for Adsorption Systems, *Journal of Hazardous Materials,* B136: 681-689. |
| [14] | Ho, Y. S.; McKay,G. (1998). A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents, *Transactions of Institute of Chemical Engineers,* 76(B): 332-340. |
| [15] | Tan, I. A. W.; Ahmad, A. L.; Hameed,B. H. (2008). Adsorption of Basic Dye on High-surface-area Activated Carbon Prepared from Coconut Husk: Equilibrium, Kinetic and Thermodynamic Studies, *Journal of Hazardous Materials,* 154: 337–346. |
| [16] | Vimonses, V.; Shaomin Lei, S.; Bo Jina, B.; Chowd, C. W. K.; Saint,C. (2009). Kinetic Study and Equilibrium Isotherm Analysis of Congo Red Adsorption by Clay Materials, *Chemical Engineering Journal,* 148:354–364. |
| [17] | Ukoha, P. O.; Nwabue, F. I.; Obasi,L. N. (2011). Solvent Extraction Studies on Copper(II) and Silver(I) Complexes of Bis(4-hydroxypent-2-ylidene)diaminoethane: Composition of Extracted Copper (II) Species, *E-Journal of Chemistry,* 8(4): 1864-1871. |
| [18] | Ukoha, P. O.; Obasi, L. N.; Nwabue,F. I. (2012). Solvent Extraction Studies on Copper(II); Silver(I) Complexes of Bis(4-hydroxypent-2-ylidene) Diaminoethane: Separation of Ag(I) from Cu(II), *International Journal of Chemistry,* 22(1): 15-24. |